The effects of defect system ordering in a weakly doped incipient ferroelectric (KTaO$_3$):

dielectric manifestation

The effects of defect system ordering in a weakly doped incipient ferroelectric (KTaO₃): dielectric manifestation

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Abstract. The temperature–frequency behaviour of the permittivity $\varepsilon'(T, f)$ and $\tan[\delta(T, f)]$ (20–300 K; 120 Hz–9 MHz), EPR, optical absorption and luminescence of KTaO₃, nominally pure and weakly doped (0.1 wt% Li; 0.01 wt% Cr; 3 wt% Cu; 1 wt% Fe; 0.1 wt% Li+0.1 wt% Cr and 0.1 wt% Li+0.1 wt% Cr+0.02 wt% Cu) were studied. Below 70 K, in all doped samples, dielectric dispersion occurs, with $\tan[\delta(T)]$ maxima positions obeying the universal Arrhenius law with activation energy $\Delta = 1000 \pm 50$ K. This is associated with local ordering in the dipole–dipole clusters containing reorienting defect pairs of various kinds, with correlations due to interaction via the TO soft mode.

1. Introduction

The high polarizabilities of SrTiO₃ and KTaO₃ incipient ferroelectrics and strong indirect dipole–dipole interaction via the TO soft mode [1–4] allow the possibility of ordering in a system of random, slowly relaxing polar defects, and induced phase transitions [3–6]. Thus, the introduction of Li, Nb or Na replacing K or Ta in KTaO₃ leads to the formation of polar, slowly relaxing complexes with an off-centre impurity as a framework. In such cases, at low impurity concentrations and low temperatures, certain tendencies to local small-scale structural orderings (distortions) have already been noted [7]. At sufficiently high concentrations of Li, Nb and Na, but lower than the 'critical' value (2.2 at.% Li [8] (0.8 at.% Li according to [9]), 0.8 at.% Nb [10] and 12 at.% Na [11]), collective dipolar freezing is observed at a certain low temperature T_g, with Fogel–Fulcher and/or stretched-exponential behaviour of the relaxation times τ (e.g. $T_g = 33$ K for 1.15 at.% Li) [12]. At concentrations of Li, Nb and Na near to or above the 'critical' value, structural phase transitions with nanodomains within large structural domains take place at certain T_c; we should mention that the existence of these phase transitions was proved for some compositions only (48 K for 2.2 at.% Li, 55 K for 3.5 at.% Li, 72 K for 5 at.% Li, etc) [7, 8, 13–16]. Nevertheless, we must stress here the absence of both a satisfactory theory and a sufficiently deep understanding of the nature of these 'random-field ferroelectrics', their structure and properties in the low-temperature phase.

Here, the question of 'precursor effects' in incipient ferroelectrics is very important. Above T_g and T_c, not only doped KTaO₃ but even undoped (i.e. nominally pure) KTaO₃ reveals the presence of temperature-dependent microregions with broken symmetry of an unclear origin [16–33].

We believe that a detailed investigation of $KTaO_3$ with low concentrations of various dopants is of interest. From this point of view we studied the dielectric spectra of nominally pure $KTaO_3$ single crystals and with admixtures of the following in the batch: 0.1 wt% Li; 0.02 wt% Cr; 3 wt% Cu; 0.1 wt% Li+0.1 wt% Cr; 0.1 wt% Li+0.1 wt% Cr+0.02 wt% Cu; 1 wt% Fe. Collateral studies of EPR, optical absorption and luminescence spectra on the same samples were carried out simultaneously.

The problem of the cooperative behaviour of off-central impurities in ferroelectrics belongs to a group of questions about the mutual interaction of defects and the order parameter. An excellent phenomenological analysis of these effects has been made by Levanuyk and co-workers [34, 35]. In our paper to interpret the experimental data it is necessary to take into consideration the specifics of the cooperative behaviour of reorienting dipoles on a microscopic level and, in particular the possibility of local ordering in pairs of reorienting dipoles, which earlier was not analysed.

2. Experimental details

Pure and metal-doped $KTaO_3$ single crystals were prepared by spontaneous crystallization from slowly cooled flux. The batch consisted of Ta_2O_5, with approximately a 20% stoichiometric excess of K_2CO_3, and a certain amount of dopant metal oxide. Crystal growth took place under an oxygen atmosphere, as the melt was cooled at a rate of $-0.5 °C$ h^{-1} from 1370 to 950 °C. In all cases the crystals were transparent and their resistivity exceeded 10^{10} Ω cm; with the exception of green $KTaO_3$:3 wt% Cu and brown-sugar-tinted $KTaO_3$:1 wt% Fe and $KTaO_3$:0.01 wt% Cr, the crystals were colourless.

Ni electrodes were evaporated onto the principal faces of {100} thin polished plates. Dielectric measurements of ε' and $\tan \delta$ were performed on a 4192 LF Hewlett–Packard impedance analyser (5 Hz–13 MHz); the sample was suspended in a He-flow cryostat allowing temperature cycling within 10–300 K at a rate of $\pm(10 - 100)$ mK s^{-1}.

EPR measurements were performed on samples of volume 1–5 mm^3. The experimental set-up consisted of an SE/X-2544 spectrometer (Radio PAN) operating at 9 GHz. We must stress that our EPR data are presented here in a very reduced form, to serve only as a tool in the sample testing, i.e. for a better understanding of the dielectric data. More exhaustive EPR results will be published elsewhere.

In addition, optical absorption and photoluminescence spectra were also studied using a Hitachi 3300 spectrophotometer and a spectrofluorometer, at 0.2–0.8 μm.

3. Dielectric spectra

No peculiarities in the temperature–frequency behaviour of ε' and $\tan \delta$ in nominally pure $KTaO_3$ have been observed. Above 30 K, the permittivity obeys the standard Curie–Weiss law $\varepsilon' = B + C(T - T_0)^{-1}$, with $B \simeq 48$, $C = 5 \times 10^4$ K and $T_0 \simeq 13$ K. At lower temperatures the saturation of permittivity connected with quantum fluctuations takes place. That is why the phase transition does not occur.

The introduction of small concentrations of different impurities results in the appearance of dielectric relaxation (figures 1–5).

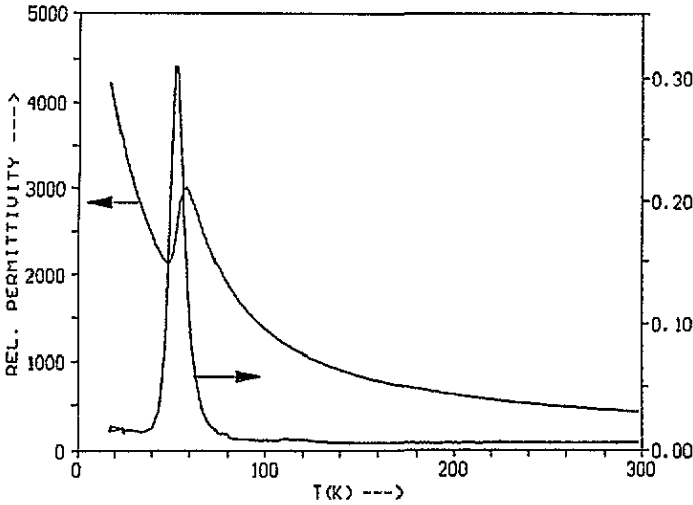The general features of the picture observed are as follows.

Figure 1. The relative permittivity and tan δ versus *T* for KTaO₃: 0.1 wt% Li+0.1 wt% Cr+0.02 wt% Cu at 40 kHz.
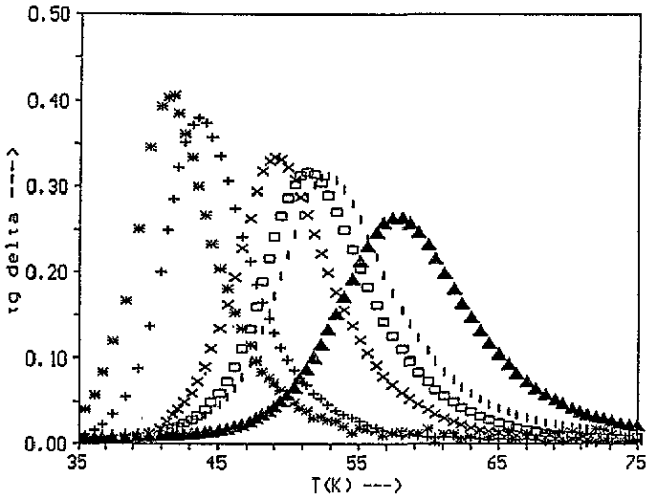

Figure 2. tan[$\delta(T)$] versus *T* for KTaO₃: 0.1 wt% Li+0.1 wt% Cr+0.02 wt% Cu at 120 Hz (*), 400 Hz (+), 4 kHz (×), 10 kHz (□), 20 kHz (|) and 100 kHz (△).

(1) The character of the dielectric dispersion is to a large degree independent of the kind of dopant(s) introduced. In all cases, the Arrhenius law is well obeyed (see figure 3).

(2) Both $\varepsilon'(T)$ and tan[$\delta(T)$] maxima positions appear at nearly the same temperature for the same frequencies, independent of the type of dopant introduced into the KTaO₃ matrix, and their (sufficiently low) concentration(s) (figures 1 and 4). This is due to almost the same values of the hopping activation energy Δ and mutually close attempt frequencies ω_0; they are typical for Li⁺ off-centres in KTaO₃ in all the samples studied (table 1).

(3) The effect observed is only weakly dependent on the defect concentration, in spite of the fact that it obviously has a 'defect' origin.
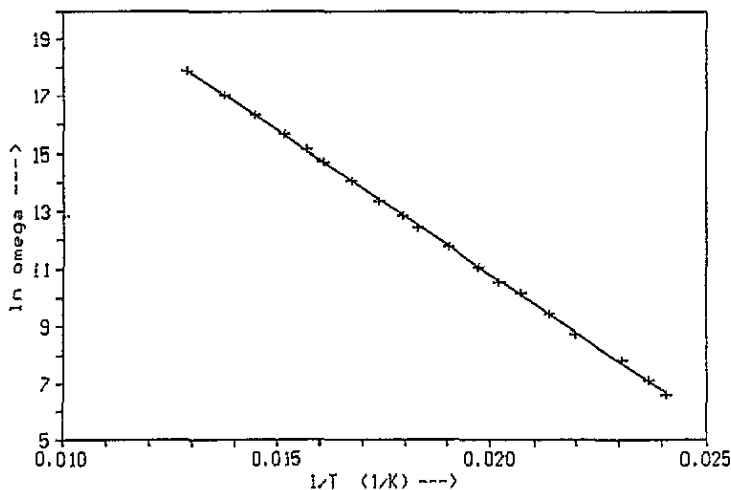
Figure 3. Arrhenius plot $\omega = \omega_0 \exp(-\Delta/T)$ for the relaxation frequency of KTaO$_3$: 0.1 wt% Li+0.1 wt% Cr. The plot was constructed from tan[$\delta(T)$] maxima positions ($f = 1592$ Hz–9 MHz). $f_0 = 9.1 \times 10^{12}$ Hz and $\Delta = 1028$ K.
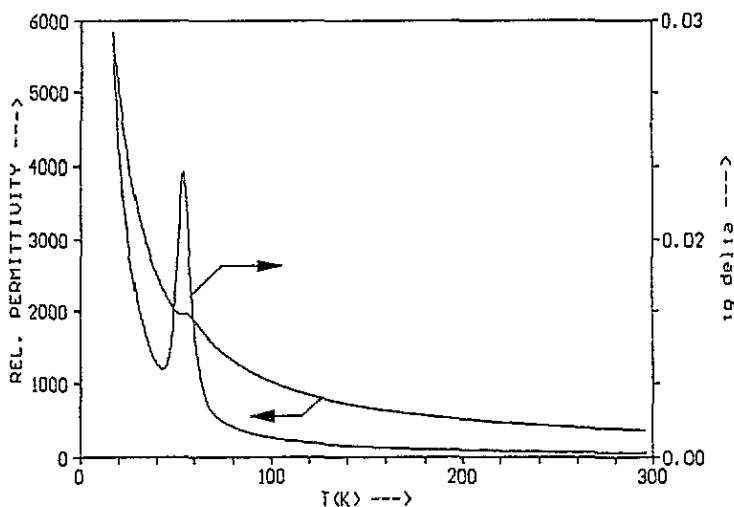

Figure 4. The relative permittivity and tan δ versus T for KTaO$_3$: 0.1 wt% Li at 40 kHz.

(4) Within the temperature region where $\omega\tau \ll 1$, for temperatures higher than tan[$\delta(T)$] maxima positions, some additional dispersion takes place, revealing the existence of a slow collective relaxation.

(5) The very high magnitudes of temperature peaks of ε' and tan δ (see figures 1 and 4) are surprising for the dopant concentrations studied. These high values can be understood only as a result of a collective phenomenon. The most pronounced (large) anomalies take place for KTaO$_3$ with acceptor dopants and for the doubly and especially the triply doped matrix, e.g. for KTaO$_3$ with Li+Cr+Cu (figure 1).
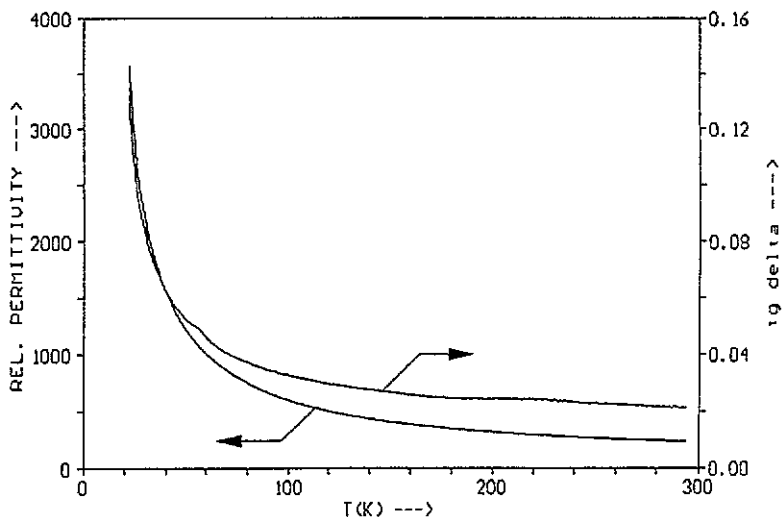
Figure 5. The relative permittivity and tan δ versus T for KTaO₃: 1 wt% Fe at 60 kHz.

Table 1. Parameters of Arrhenius relaxation for a series of weakly doped KTaO₃ single crystals.

Dopants in KTaO₃ (wt% in batch)	f_0 (Hz)	ω_0 (s⁻¹)	Δ (K)
0.1 Li	5.2×10^{12}	3.3×10^{13}	1010
0.02 Cr	1.1×10^{13}	6.9×10^{13}	1051
3 Cu	2.2×10^{13}	1.4×10^{14}	1065
1 Fe	2.6×10^{12}	1.6×10^{13}	1052
0.1 Li+0.1 Cr	9.1×10^{12}	5.7×10^{13}	1028
0.1 Li+0.1 Cr+0.01 Cu	3.3×10^{12}	2.1×10^{13}	1000

Also, an additional smooth temperature maximum of losses was observed for KTaO₃: Cu and for KTaO₃: Li+Cr+Cu samples (figure 1); within the frequency range studied, these maxima occur in the temperature range from 100 to 130 K and obey the Arrhenius law with an activation energy of 2500–2600 K.

4. Local ordering effect in a system of interacting relaxators of different natures and dielectric relaxations: the model

The model that we propose is based on the interaction effect via the TO soft optical mode of two different relaxators. We start with a discussion of the dynamics of dipole pairs.

Let r be the distance between dipoles d_{1m} and d_{2n}; r_c is the correlation radius of the ferroelectric order parameter ($r_c = v^{1/2}\omega_0^{-1}$; ω_0 is the frequency of the soft TO mode at $q = 0$; v is a parameter of TO-mode dispersion). The Hamiltonian of the indirect dipole–dipole interaction via the soft TO mode can be written as [1, 2]

$$H_{d-d}^{(1,2)} = \sum_{ijmn} d_{1m} d_{2n} \gamma_{mi}^{(1)} \gamma_{nj}^{(2)} F_{ij} \qquad (1)$$

where

$$F_{ij} = \frac{-(\varepsilon - \varepsilon_\infty)}{16\pi^2} \left\{ \frac{2}{3} \frac{\exp(-r/r_c)}{rr_c^2} \delta_{ij} \right.$$

$$\left. + (3n_i n_j - \delta_{ij}) \left[\frac{1}{r^3} - \exp\left(\frac{-r}{r_c}\right) \left(\frac{1}{r^3} + \frac{1}{r^2 r_c} + \frac{1}{3rr_c^2} \right) \right] \right\}. \tag{2}$$

Here the symbols m, n correspond to x, y and z projections, $n_i = r_i/r$, ε_∞ is the high-frequency dielectric susceptibility, F_{ij} characterizes the indirect dipole–dipole interaction and γ_{mi} is the local field factor (obvious long-range electrostatic interactions of Lorentz type, the important Born–Mayer short-range interactions and covalency effects contribute to this).

In the case of a system of off-centre impurity ions with deep wells (as in KTaO$_3$:Li), we are dealing with the possibility of distribution of ions among localized states in single wells (six wells for KTaO$_3$:Li). That is why we have six possible orientations of the off-centre ion dipole. The distribution among such discrete dipole orientations is determined by cooperative effects, in accord with (1) and (2). It is usual to use the pseudo-spin description in this case. For simplicity, we use the pseudo-spin $S = \frac{1}{2}$, i.e. we consider the reorientations of each dipole in a double-well potential. In this simple case the Hamiltonian of the indirect dipole–dipole interaction based on (1) and (2) can be written as

$$H = -\hbar J(T, r) \sigma_z^{(1)} \sigma_z^{(2)} \tag{3}$$

where $\sigma_z^{(1)}$ and $\sigma_z^{(2)}$ are Pauli matrices describing orientations of dipoles 1 and 2, and $J(T, r)$ is the interaction amplitude. In (3), $J(T, r) \sim F_{zz}(T, r)$, where $F_{zz}(T, r)$ corresponds to (1) and (2), and the two dipole orientations are parallel to [001] and [00$\bar{1}$]. Let us show that, because of firstly the softness of the incipient ferroelectric lattice, secondly the high value of local fields (the local field factor $\gamma \gg 1$ at certain sites) and thirdly the significant magnitudes of the activation energies for actual dipolar defects, there is a universal mechanism of local ordering in dipole clusters at low concentrations of dipolar centres of different types, which manifests itself by a cusp in $\varepsilon'(T)$ and by a maximum in $\tan[\delta(T)]$.

From (1) and (2) it follows that $J(T, r)$ rises quickly with $1/\omega_0$, being significantly large, and decreases slowly with increasing distance as $1/r$, at $r \leqslant r_c$. Indeed, the r_c-value increases with increasing $1/\omega_0$, which leads to an increase in $J(T, r)$, in agreement with (2). On the other hand, the main role in (2) belongs to the Ornstein–Zernicke terms for $r \ll r_c$. The latter leads to an uncommon spatial dependence of the dipole–dipole interaction in the situation when it reaches critical strengthening [1]. We consider that the relaxing pairs meet these requirements exactly. The system of linear differential equations for two bonded relaxators with relaxation rates $1/\tau_1$ and $1/\tau_2$ and interaction J are

$$\dot{P}_1 = -\frac{1}{\tau_1} P_1 + J P_2$$

$$\dot{P}_2 = -\frac{1}{\tau_2} P_2 + J P_1 \tag{4}$$

where P_1 and P_2 are the mean values of the relaxing dipole moments. The solution for (4) yields a bonded relaxator system with two relaxation rates $1/\tau_\mp$:

$$\frac{1}{\tau_\mp}(T) = \frac{1}{2} \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} \right) \mp \left[\frac{1}{4} \left(\frac{1}{\tau_1} - \frac{1}{\tau_2} \right)^2 + [J(T)]^2 \right]^{1/2}. \tag{5}$$

It follows from (5) that at

$$[J(T, r)]^2 = \frac{1}{\tau_1}(T)\frac{1}{\tau_2}(T) \tag{6}$$

$(1/\tau_-)(T) = 0$, corresponding to a peak of static dielectric permittivity for a pair of electric dipoles interacting via the soft TO mode. Equation (6) is useful to find the temperature T_0 for ordering in dipole pairs and the corresponding maximum of $\varepsilon'(T)$. At small ω, the peak in the temperature dependence of the imaginary part $\varepsilon''(T)$ of the dielectric permittivity will be slightly displaced with respect to $\varepsilon'(T)$ on the temperature axis, since its position is given by $(1/\tau_-)(T) = \omega$. However, the peak of $\tan[\delta(T)]$ corresponds exactly to the $\tau_-(T)$ peak position.

Such critical behaviour in dipole clusters (6) could be met for clusters (distances between dipole pairs) where $J(T, r) > U$ (U describes the action of an internal static field of non-reorientable centres). Because U is usually large even in nominally pure systems, $J > U$ holds only for dipoles with $r \leqslant r_c$; this, together with (6), lifts the limitations on the τ_1^{-1} and τ_2^{-1} properties at which local ordering may occur. Really, according to (2), in the region where (6) holds, $J(T, r) \sim r^{-1}$, i.e. $J(r)$ is a very weak function of r. From this point of view, almost all the functions of J^2 coincident with $(1/\tau_1)(T)(1/\tau_2)(T)$ at a certain $r \leqslant r_c$, fulfilling (6), and greater than U^2 will allow ordering within the region $r < r_c$. The values of the relaxation rate parameters of individual dipoles are thus restricted. If $1/\tau_i = (1/\tau_i)\exp(-\Delta_i/T)$, then (for dipole–dipole ordering effects connected with the peak in $\varepsilon'(T)$) the values of $(1/\tau_1^{(0)})(1/\tau_2^{(0)})$ and $\Delta_1 + \Delta_2$ have to be neither too large nor too small. Owing to a rapid (exponential) rise in $(1/\tau_1)(T)(1/\tau_2)(T)$ and the restriction on the magnitude of r from above, the temperatures T_0 of local ordering for dipole pairs composed of the same couple of partners but located at a different distances $r \leqslant r_c$ would be close to each other. Indeed the equation for T_0 has the form

$$J^2 = \frac{1}{\tau_1^{(0)}} \frac{1}{\tau_2^{(0)}} \exp\left(-\frac{\Delta_1 + \Delta_2}{T_0}\right). \tag{7}$$

From (7), for the temperature of local ordering we obtain

$$T_0 \simeq \frac{\Delta_1 + \Delta_2}{\ln[1/J^2\tau_1^{(0)}\tau_2^{(0)}]}. \tag{8}$$

$T_0(r)$ is a very weak function of r in the actual region $r < r_c$, where $J(r) \sim r^{-1}$. The values $\tau_1^{(0)}$ and $\tau_2^{(0)}$ are governed by the larger of the values of Δ_i. This results in a very narrow temperature interval δT, where the resulting soft relaxation mode is realized. Let us consider a situation when the same kind of leading dipole exists in each dipole pair. For this leading dipole the inequality $\Delta_1 \gg \Delta_2$ is fulfilled; Δ_2 belongs to the second dipole in the pair. As a result we immediately have from (8)

$$\delta T \approx T_0 \Delta_1^{-1} \delta\Delta_2 \tag{9}$$

where we have neglected the weak dependence of T_0 on $\tau_2^{(0)}$ and J. For a reasonable value of $\delta\Delta_2 \simeq \Delta_2$ and $\Delta_1 \gg \Delta_2$, the condition $T \ll T_0$ from (9) is met.

5. Discussion, possible reorienting centres and spectroscopic data

5.1. Dielectric behaviour

We think that the pair approximation for real dipole clusters is a good approach in our attempt to describe the behaviour of the system at low concentrations of polar defects and actual values of r_c.

The smooth character of the $J(r)$ dependence in the actual region $r < r_c$ thus leads to the possibility of summing the pair contributions to the resulting dielectric permittivity, with almost identical contributions of individual pairs with different $r < r_c$.

Consequently, at least for identical types of pairs, a narrow peak in the dielectric permittivity in the region of dipole–dipole ordering in pairs with $r < r_c$ is formed. It can be seen that the pair interaction between identical off-centred ions (e.g. Li^+) could not lead to the effects observed since the value of Δ_{Li} is too high. Dipole ordering could be realized in pairs of Li^+ with dipole centres with comparably small values of τ_0 and Δ. The situation that we encounter in our samples is as follows: Li^+ (present in a low concentration) is the leading participant of the pairing process in all the doped crystals that we studied, and other centres (having comparably low values of $\tau_i^{(0)}$ and Δ_i) form pairs with it. Thus the positions of $[\varepsilon'(T)]_{max}$ and $\tan\delta\{[(T)]_{max}\}$ on the temperature axis are coincident to good accuracy.

Thus, within the framework of the model developed, our dielectric spectroscopy data are explained as a result of local ordering in dipole–dipole clusters, which contain reorienting defect pairs of various kinds. The existence of one leading defect in relaxing pairs leads to a very narrow temperature interval for local ordering in pairs in all the materials under study. The character and magnitude of dielectric response, however, depend strongly on the concentration of interacting dipole moments of the impurity introduced, on the magnitudes of their dipole moments and on the character of the indirect dipole–dipole interaction. For example, in $KTaO_3$:0.1 wt% Li as can be seen from figure 4 we observed a sharp increase in the dielectric permittivity as the temperature decreased to 20 K. It is connected with a contribution of the TO mode, whose frequency decreases with decreasing temperature. In this case, the effect of dipole–dipole Li^+–Li^+ (impurity) correlations leads to a small contribution to ε', because both off-centres are ions located in the K^+ sites in the $KTaO_3$ lattice. Indeed, as follows from calculations of a local field factor γ, in these sites $|\gamma_i| \ll 1$, which corresponds to a decrease in the dipole–dipole interaction: $H_{dd} \sim \gamma_i^2$. However, if a reorienting defect of another kind with a comparatively small activation energy appears on Ta^{5+} or O^{2-} sites, the situation changes drastically. We shall here have $\gamma_2 \gg 1$; consequently, a strong increase in the amplitude of the dipole–dipole interaction potential occurs: $H_{dd} \sim \gamma_1 \gamma_2$. The value of $|\gamma_1 \gamma_2|$ can be one or two orders of magnitude higher than γ_1^2. In this case of not too weak a concentration of dipoles of a different type the appearance of an additional peak can be expected in the temperature behaviour of ε' over the TO-mode background contribution. In $KTaO_3$:0.1 wt% Li+0.1 wt% Cr+0.02 wt% Cu this situation *is realized (figure 1). Here oxygen vacancies, compensating for the appearance of Cr ions,* can be reorienting dipole centres of the second kind (e.g. oxygen vacancies with a trapped electron). Thus, the concentration of dipoles of the different types (i.e. centres connected with the vacancies) correlates with the Cr admixture concentration (about 0.1 wt%) and as a result may have a value close to the Li^+ dipole concentration.

Relaxators could consist of not only reorientable electric dipole moments but also reorientable electric quadrupole and reorientable elastic dipole moments. In this case, the phenomenon is qualitatively the same, but the details of pair interaction via the soft TO mode and elastic TA mode and the expression for $J(r, T)$ change [36, 37], although

Table 2. The concentrations of selected centres, as determined from EPR measurements.

Sample	Centre	Concentration (at.%)	Remarks
KTaO₃:1 wt% Fe	Tetragonal Fe^{3+}	$\geqslant (1/5) \times 10^{-3}$	Fe^{3+} clusters probably exist
	Cubic Fe^{3+}	$\geqslant (1/5) \times 10^{-4}$	
KTaO₃:0.1 wt% Li+0.1 wt% Cr+Cu	Tetragonal Cu^{2+}	$(1-10) \times 10^{-5}$	—
	Cubic Fe^{3+}	$\leqslant 10^{-6}$	

the $J(r)$ dependence remains weak at $r \ll r_c$. As was shown in [36, 37], in describing this 'interfering' indirect interaction it is important to take into account the electrostrictive anharmonic interaction and bilinear interaction of deformations with polarization gradients.

An estimation of the correlation effects on $\tan\delta$ behaviour could be made using an expression connecting $\tan\delta$ and ε' with dipole concentration N and dipole polarizability α. If ε_0' (the contribution to ε' not connected with defect dipoles) obeys the inequality $\varepsilon_0' \gg 4\pi\alpha N/(1+\omega^2\tau^2)$, then

$$(\tan\delta)_{max} = \left.\frac{\varepsilon_0''}{\varepsilon_0'}\right|_{T=T_{max}} + \frac{2\pi\alpha N}{\varepsilon_0'|_{T=T_{max}}}. \tag{10}$$

From this,

$$2\pi\alpha N = \varepsilon_0'|_{T=T_{max}}[(\tan\delta)_{max} - (\tan\delta)_0|_{T=T_{max}}]. \tag{11}$$

Here T_{max} is the temperature at which the maximum of $\tan[\delta(T)]$ lies; $(\tan\delta)_0|_{T=T_{max}}$ is the loss without the contribution of paired dipoles. Using equation (11) we have obtained from our experiments $\alpha_1 N_1 \simeq 75.5/2\pi$ and $\alpha_2 N_2 \simeq 84.5/2\pi$ for KTaO₃:Cr and KTaO₃:Li+Cr, respectively, which are almost identical values (!).

The relaxators with activation energy 2500–2600 K that we observe in KTaO₃: Li+Cr+Cu and KTaO₃:Cu could be interpreted as a manifestation of a correlated hopping process in Li–Li pairs (i.e. two dipole reorientations between two ferroelectrically ordered pair states).

5.2. EPR spectra

EPR spectra of samples of the same KTaO₃ crystals used in dielectric relaxation studies have been investigated in order to identify the reorienting dipole and quadrupole paramagnetic centres.

All the KTaO₃ samples revealing $\varepsilon'(T)$ and/or $\tan[\delta(T)]$ anomalies yield EPR signals. In these cases, the following paramagnetic centres were observed: cubic Fe^{3+} [38], tetragonal Fe^{3+} [39, 40] and tetragonal Cu^{2+} [41, 42]. The concentrations of these paramagnetic centres estimated from the EPR data are presented in table 2. In KTaO₃: 0.1 wt% Li+0.1 wt% Cr+0.01 wt% Cu the EPR spectrum of Cu^{2+} axial centres with parameters close to those in [41, 42] dominated (figure 6). The total concentration of Cu^{2+} centres was $10^{17}-10^{18}$ cm^{-3}. The most plausible model for this centre is a Cu^{2+} ion replacing Ta^{5+}, with an oxygen vacancy ($V_O \equiv V_{O^{2-}}$) in the first coordination sphere. Let us remember that the $Cu^{2+}-V_O$ centre can have a double-minima potential along the defect axes [37]. Such a potential can arise because the Coulomb, polarization and Born–Mayer forces are not balanced owing to the presence of a vacancy and under the action of a quadratic Jahn–Teller effect and a linear pseudo-Jahn–Teller effect on polar distortions. Hopping transitions between two of these potential wells lead to a modulation of the dipole moment of the centre.
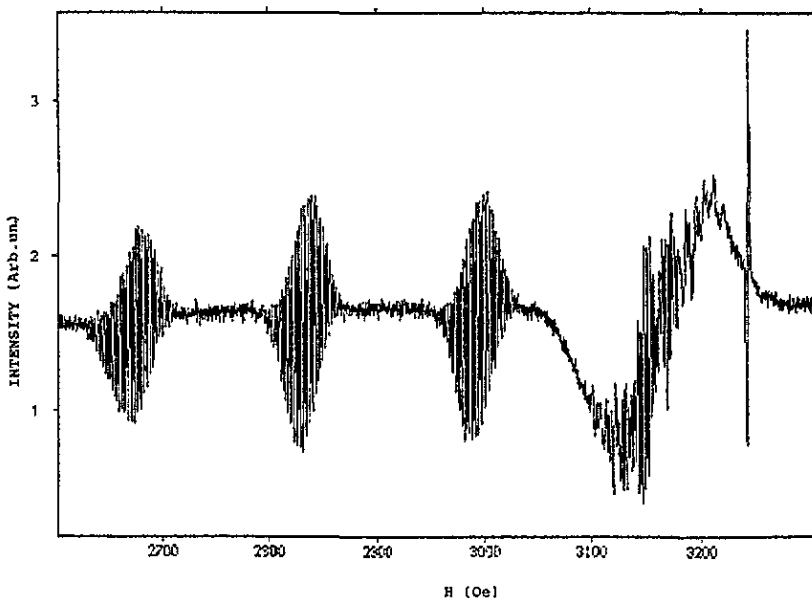
Figure 6. Tetragonal EPR spectrum of a $KTaO_3$:Li, Cr, Cu^{2+} single crystal. The four lines of hyperfine structure are due to ^{63}Cu and ^{65}Cu (both $I = \frac{3}{2}$). Superfine lines are clearly evident [43, 45].

The analysis performed indicates the probable existence of centres with reorienting dipolar and quadrupole degrees of freedom (the probable candidates are Cu^{2+}–V_O and one of two types of tetragonal Fe^{3+} centres with possible hole–bipolaron nature [37]) which could interact with dipole reorienting centres of another type (e.g. with off-centre impurity non-paramagnetic ions Li^+, Na^+ and Nb^{5+} in $KTaO_3$) and participate in forming the considered mechanism of dielectric anomalies.

5.3. Optical absorption and photoluminescence

The same conclusion can be arrived at from optical absorption and photoluminescence data. As in EPR measurements, the samples, where the discussed dielectric dispersion is absent (nominally pure $KTaO_3$), reveal no optical spectroscopy active defects. The optical absorption and photoluminescence spectra (77 K) of $KTaO_3$:Cu have a corresponding absorption band and luminescence line with a maximum at about 680 nm which, following [29], is connected with Ta^{3+}–V_O. A similar absorption band connected with Ta^{3+}–V_O was also observed in the optical absorption of $KTaO_3$:Li+Cr+Cu. Let us remember that Ta^{3+} ($3d^2$) in this state is a pseudo-Jahn–Teller ion [37]. Owing to the vibronic effects, the creation of a multiwell potential and associated reorienting dipole and quadrupole moments is extremely probable.

A weak band in the optical absorption and photoluminescence spectra occurred in the region 740–750 nm. Following [43, 44], this could be connected with a Cr^{3+} ion in an octahedral position. The optical absorption spectrum of $KTaO_3$:Fe has a very weakly pronounced band in the region 710–760 nm, which is also probably connected with the presence of uncontrolled octahedral Cr^{3+}. Typical luminescence (if it were present) would be masked by stronger wider luminescence bands spanning from 600 to 800 nm, with a maximum at 780 nm.

In $KTaO_3$:Cr, Ta^{3+}–V_O centres are revealed as a wide-band optical absorption with a maximum at 680 nm at room temperature (figure 7). These samples have been investigated earlier [43, 44] where photoluminescence in the near-IR region with a maximum zero-phonon line at 746 nm (at 92 K) was associated with the optical transitions of octahedral Cr^{3+}. Although the octahedral Cr^{3+} centre at the Ta^{5+} site is not dipolar, oxygen vacancies or localized holes (O^- centres) can arise near such a Cr^{3+} centre because of charge compensation. Oxygen vacancies can possess a reorienting electric dipole moment, for instance, in the case of the electron trapped by the vacancy and localized at one of the two Ta ions nearest to the vacancy. Localized holes also can have a reorienting electric dipole moment, owing to the pseudo-Jahn–Teller effect.
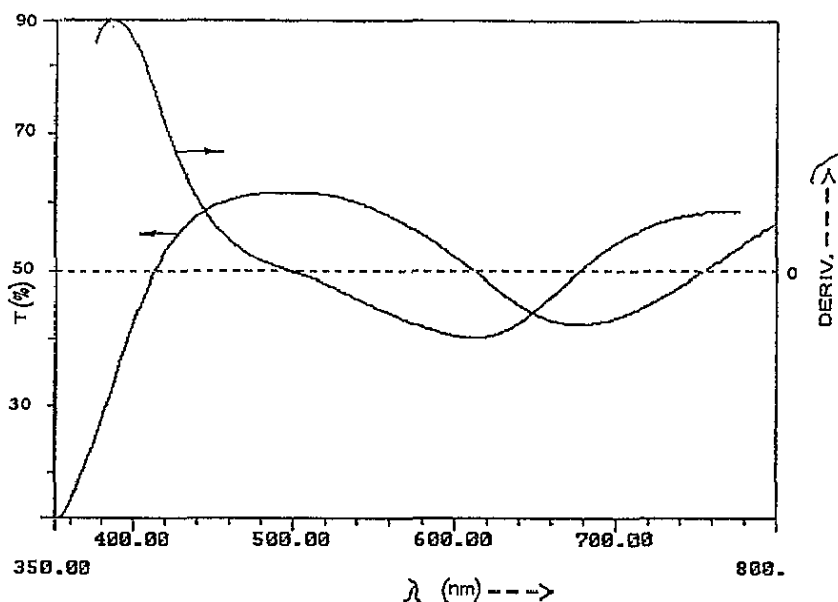

Figure 7. Optical transmission and its derivative for $KTaO_3$:0.01 wt% Cr. $T = 293$ K; the sample thickness was 0.2 mm.

5.4. The centres

Let us emphasize now which centres could have reoriented electrical dipole and quadrupole moments in $KTaO_3$. Apart from the obvious contribution of the Li^+, Na^+ and Nb^{5+} off-centres here, other types of centre could play an important role. These are the pseudo-Jahn–Teller Cu^{2+}–V_O and Ta^{3+}–V_O centres, where reorientations of the electric dipole moment take place in an asymmetric two-well potential [37]. Also, the strong Jahn–Teller effect on the Fe^{2+} ion can also lead to the situation under discussion at reorientations between energetically equivalent configurations. Finally, hole and bihole centres bound to the paramagnetic centre must be taken into account as possible reorienting units. First this could be Fe^{3+}–O^-, where the hole on the oxygen ion can reorient between its six positions in the first coordination sphere. Another actual situation is the hole bipolaron, localized near the paramagnetic centre. An example of this centre could be the O^-–Fe^{3+}–O^- centre, where both axial and rhombic states can occur [37]. Whereas the axial state possesses a

quadrupole reorienting moment only, the rhombic state has a dipole reorienting moment too. Let us note also that two types of $O^--Fe^{3+}-O^-$ bipolaron centres could be related [37] to the Fe^{3+} axial and rhombic [45] centres observed in $KTaO_3$.

We conclude that the following centres can possess dipole and quadrupole degrees of freedom that could interact with dipole reorienting centres of another kind (e.g. with the off-centre non-paramagnetic ions Li^+, Na^+ and Nb^{5+}) and participate in forming the dielectric dispersion considered: Fe^{2+}, $Fe^{3+}-O^-$ exchange pairs, $O^--Fe^{3+}-O^-$ bipolarons (in $KTaO_3$:Fe); axial $Cu^{2+}-V_O$ (in $KTaO_3$:Cu and $KTaO_3$:Li+Cr+Cu); $Ta^{3+}-V_O$ (in $KTaO_3$:Cu, $KTaO_3$:Li+Cr+Cu and $KTaO_3$:Cr); O^--defect pairs and oxygen vacancies with trapped electrons ($KTaO_3$: Cr^{3+} and $KTaO_3$: Fe^{3+}).

6. Conclusions

The model presented describes qualitatively the uncommon dielectric dispersion observed and explains it as a result of local ordering in dipole clusters of defects of different kinds, with correlations mediated by an indirect interaction via the soft TO mode. The general uniformity of the effect observed, i.e. very close coincidence of temperature positions of peculiarities of $\varepsilon'(T)$ and $\tan[\delta(T)]$ in all the $KTaO_3$ samples with a low concentration of impurities of different kinds, is attributed as follows.

(1) All the samples investigated contain at least two types of interacting and reorienting dipolar defect.

(2) All the defects under consideration occupy sites with a low local symmetry; this both increases significantly the local field factor magnitude and enhances the dipole–dipole interaction.

(3) The low frequencies of the soft TO mode in the temperature region in question enhance the indirect dipole–dipole interaction, and its spatial dependence changes in comparison with the common law.

(4) These dipole pairs (or clusters) with an average distance of the order of the correlation radius or less have soft cooperative relaxator modes.

Let us stress that our model requires the magnitude of activation energy for hopping *reorienting moment of one 'principal' relaxator to be predominant in pairs of different kinds.* Thus paired indirect interaction via the TO mode provides critical cooperative slowing down of relaxations in different dipolar clusters (in the simplest case in pairs) within a narrow specific temperature region, in which the dielectric relaxation takes place.

The local ordering of different reorienting defects in dipole–dipole clusters is one of the possible causes of the appearance of correlated microregions, often encountered in nominally pure $KTaO_3$.

In samples revealing dielectric relaxation, $Ta^{3+}-V_O$ and $Cu^{2+}-V_O$ centres, $Fe^{3+}-O^-$ exchange pairs and $O^--Fe^{3+}-O^-$ axial and rhombic bipolarons are the most probable candidates for dipole and quadrupole relaxing defects that can participate in ordering with Li^+ as the 'leading' relaxator. Let us mention that the introduction of additional acceptor impurities (of either one or several kinds) undoubtedly leads to an increase in the O^- centre and oxygen vacancy concentration. This in turn should enhance dielectric relaxation, which is actually observed.

Acknowledgments

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